

Supporting Information

Organic Dyes Containing Furan Moiety for High-Performance Dye-Sensitized

Solar Cells

Jiann T. Lin,^{*a} Pin-Cheng Chen,^b Yung-Sheng Yen,^a Ying-Chan Hsu,^a Hsien-Hsin

Chou,^a and Ming-Chang P. Yeh^{*b}

^a Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115. ^b Department of

Chemistry, National Taiwan Normal University, Taipei, Taiwan 115.

E-mail: jtlin@chem.sinica.edu.tw

Experimental Methods

General Information. Unless otherwise specified, all the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified by standard procedures, or purged with nitrogen before use. ^1H NMR spectra were recorded on a Bruker 400-MHz or 500-MHz spectrometer. Absorption spectra were recorded on a Cary 50 probe UV-Vis spectrophotometer. All chromatographic separations were carried out on silica gel (60M, 230-400 mesh). Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. The preparation of TiO_2 precursor and the electrode fabrication were carried out based on previous report¹ with an autoclaved temperature of 240 °C. The film thickness measured by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA) was about 15 μm . The TiO_2 electrode with a 0.25 cm^2 geometric area was immersed in a acetonitrile/tert-butanol mixture (volume ratio 1:1) containing 3×10^{-4} M cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719, Solaronix S.A., Switzerland) or in the THF solution containing 3×10^{-4} M organic sensitizers for overnight. A platinized FTO was used as a counter electrode and was controlled to have an active area of 0.36 cm^2 by adhered polyester tape with thickness of 60 μm . After rinsing with CH_3CN or THF, the photoanode was placed on top of the counter

electrode and tightly clipping them together to form a cell. Electrolyte was then injected into the space and then sealing the cell with the Torr Seal cement (Varian, MA, USA). The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I₂), and 0.5 M 4-tert-butylpyridine (TBP) dissolved in acetonitrile. A 0.6 × 0.6 cm² cardboard mask was clipped onto the device to constrain the illumination area. The photoelectrochemical characterizations on the solar cells were carried out by using a modified light source, 300 W Xe lamp (Oriel 6258) equipped with a water-based IR filter and AM 1.5 filter (Oriel 81080 kit). Photocurrent-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc., USA) at a light intensity of 100 mW/cm² measured by a thermopile probe (Oriel 71964). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at short circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW/cm². The photovoltage transients of assembled devices were recorded with a digital oscilloscope (LeCroy, WaveSurfer 24Xs). Pulsed laser excitation was applied by a Q-switched Nd:YAG laser (Continuum, model Minilite II) with 1 Hz repetition rate at 532 nm and a 5 ns pulse width at half-height. The beam size was slightly larger than 0.5 × 0.5 cm² to cover the area of the device with an incident energy of 1 mJ/cm². The

recombination lifetime of photoinjected electrons with oxidized dyes was measured by transient photovoltages at open circuit with the presence of LiI electrolyte (0.5 M). The average electron lifetime can be estimated approximately by fitting a decay of the open circuit voltage transient with $\exp(-t/\tau_R)$, where t is time and τ_R is an average time constant before recombination.

Synthesis of materials

(4-(Diphenylamino)benzyl)triphenylphosphonium bromide (**1a**)², 4-(diphenylamino)-phenylboronic acid (**2a**)³, 9,9-diethyl-*N,N*-diphenyl-7-(5-(tributylstannyl)thiophen-2-yl)-9*H*-fluoren-2-amine (**3a**)⁴, ((7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)-methyl)triphenylphosphonium bromide (**4a**)² were prepared according to the literature procedure.

4-(2-(Furan-2-yl)vinyl)-*N,N*-diphenylaniline (**1b**)

(4-(Diphenylamino)benzyl)triphenylphosphonium bromide (**1a**) (1.67 mmol, 1 g) THF (22 mL) and *t*-BuOK (1.69 mmol, 0.19 g) was stirred at ambient temperature under nitrogen atmosphere for 1 h. 2-furaldehyde (1.77 mmol, 0.17 g) was dissolved in THF and added dropwise to the solution, and the reaction mixture was stirred for 1 h at ambient temperature, whereupon the mixture was heated to reflux for 24 h. The reaction mixture was allowed to cool to ambient temperature and a molar excess of water was added. The organic layer was extracted with CH₂Cl₂, washed with brine. The organic extract was dried over anhydrous MgSO₄ and evaporated under vacuum.

The crude product was used in the next step without further purification.

5-(4-(diphenylamino)styryl)furan-2-carbaldehyde (1c)

A mixture of **1b** (0.79 g, 2.34 mmol) and THF was cooled to -78 °C using acetone-liquid N₂ bath. *n*-Butyl lithium (1.75 mL, 1.6 M solution in hexanes, 2.81 mmol) was added dropwise over 10 min with vigorous stirring. It was brought to 0 °C during 1 h and kept at this temperature for additional 1 h. Again the mixture was cooled to -78 °C and DMF was added at once. The solution was brought to room temperature and stirred overnight. The reaction was quenched by 1 N HCl and extracted with diethyl ether. The combined organic extract was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to yield the crude product as an orange solid. It was purified by column chromatography on silica gel using hexane/CH₂Cl₂ mixture (1:1) as eluent to give **1c** as a yellow-orange solid. ¹H NMR (400 MHz, acetone-*d*₆): δ 9.59 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 3.7 Hz, 1H), 7.34 (m, 5H), 7.10 (m, 6H), 7.06 (d, *J* = 16.3 Hz, 1H), 7.00 (m, 2H), 6.72 (d, *J* = 3.7 Hz, 1H). MS (FAB) *m/z*: 365.1 (M⁺).

(*E*)-2-Cyano-3-(5-(4-(diphenylamino)styryl)furan-2-yl)acrylic acid (1)

To a flask containing a mixture of **1c** (0.44 g, 1.20 mmol), cyanoacetic acid (0.12 g,

1.41mmol), ammonium acetate (0.030 g, 0.39 mmol) was added acetic acid (10 mL). The mixture was heated at 100 °C for 8 h. and allowed to cool to room temperature. The resulting solid was filtered and washed with distilled water, diethyl ether and methanol to give a dark brown solid. The pure product was obtained by silica gel chromatography to afford **1**. ^1H NMR (500 MHz, acetone- d_6): δ 7.99 (s, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.45 (d, J = 3.4 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.13 – 7.08 (m, 6H), 7.00 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, THF- d_8): δ 164.4, 160.4, 149.6, 149.1, 148.4, 137.9, 134.2, 131.1, 130.2, 129.1, 125.9, 125.2, 124.4, 123.5, 116.7, 113.8, 112.7, 112.6, 98.5. MS (FAB) m/z : 432.1 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_3$: C, 77.76; H, 4.66; N, 6.48. Found: C, 77.46; H, 4.76; N, 5.98.

5-(4-(Diphenylamino)phenyl)furan-2-carbaldehyde (2b)

A stirred mixture of 4-(diphenylamino)phenylboronic acid (1.11 g, 3.83 mmol), 5-bromofuran-2-carbaldehyde (0.60 g, 3.45 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.044 g 0.038 mmol) in toluene/ethanol (50/5 mL) and 2M aqueous Na_2CO_3 solution (3 equiv.) was added via syringe. The reaction mixture was heated to 85 °C for 24h. The product was extracted with CH_2Cl_2 , wash with water, and dried over MgSO_4 . After evaporation of the solvent, the residue was purified by chromatography on silica gel by eluting with

Hexane/dichloromethane to afford **2b**. ¹H NMR (400 MHz, acetone-*d*₆): δ 9.61 (s, 1H), 7.77 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.50 (d, *J* = 4.0 Hz, 1H), 7.38 – 7.34 (m, 4H), 7.15 – 7.12 (m, 6H), 7.06 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.02 (d, *J* = 3.6 Hz, 1H). MS (FAB) *m/z*: 339.1 (M⁺).

(*E*)-3-(5-(4-(Diphenylamino)phenyl)furan-2-yl)-2-cyanoacrylic acid (2)

It was synthesized by the same procedure as described above for **1**. ¹H NMR (400 MHz, acetone-*d*₆): δ 8.02 (s, 1H), 7.86 (m, 2H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.37 (m, 4H), 7.15 (m, 6H), 7.13 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, THF-*d*₈) δ 164.4, 160.8, 150.3, 148.8, 148.1, 138.1, 138.0, 130.4, 127.3, 126.2, 125.8, 124.8, 123.2, 122.9, 116.7, 108.7, 108.6, 97.9. MS (FAB) *m/z*: 406.1 (M⁺). Anal. Calcd for C₂₆H₁₈N₂O₃: C, 76.83; H, 4.46; N, 6.89. Found: C, 76.46; H, 4.50; N, 6.55.

5-(5-(7-(Diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)thiophen-2-yl)furan-2-carbaldehyde (3b)

A mixture of 5-bromofuran-2-carbaldehyde (0.92 g, 5.26 mmol), 9,9-diethyl-*N,N*-diphenyl-7-(5-(tributylstannyl)thiophen-2-yl)-9*H*-fluoren-2-amine (**3a**) (4.00 g, 5.26 mmol), Pd(PPh₃)₄ (0.06 g, 0.053 mmol) and dry DMF were placed into two-necked flask under nitrogen atmosphere and stirred overnight at 100 °C.

After cooling, it was quenched with aqueous KF and extracted with diethyl ether. The organic extracts were washed with brine solution and dried over anhydrous MgSO₄. The crude product was purified by column chromatography using a dichloromethane / hexane mixture as eluent to give **3b** as a yellow-orange solid. ¹H NMR (400 MHz, THF-*d*₈): δ 7.98 (s, 1H), 7.72-7.63 (m, 5H), 7.53 (d, *J* = 3.9 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.25-7.21 (m, 4H), 7.14 (d, *J* = 1.9 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 4H), 7.03-6.98 (m, 3H), 6.94 (d, *J* = 3.8 Hz, 1H), 2.04-1.95 (m, 4H), 0.38 (t, *J* = 7.3 Hz, 6H). MS (FAB) *m/z*: 565.2 (M⁺).

(*E*)-2-Cyano-3-(5-(5-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)-thiophen-2-yl)furan-2-yl)acrylic acid (3)

It was synthesized by the same procedure as described above for **1**. ¹H NMR (400 MHz, THF-*d*₈): δ 7.98 (s, 1H), 7.72-7.63 (m, 5H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 1H), 7.26-7.22 (m, 4H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.10-7.09 (m, 4H), 7.04-6.97 (m, 3H), 6.94 (d, *J* = 3.6 Hz, 1H), 2.08-1.90 (m, 4H), 0.38 (t, 6H). ¹³C NMR (100 MHz, THF-*d*₈): δ 164.2, 161.9, 161.3, 161.0, 155.5, 152.4, 151.7, 149.0, 148.9, 148.5, 142.9, 138.7, 137.1, 132.8, 131.0, 129.3, 127.8, 126.7, 126.1, 125.9, 125.7, 125.2, 124.3, 124.1, 123.6, 122.7, 122.4, 122.3, 121.4, 121.3, 120.7, 119.7, 119.2, 116.4, 110.6, 108.8, 98.7, 57.1, 33.3, 32.0, 9.6, 8.6, 8.3. MS (FAB) *m/z*: 632.2 (M⁺).

Anal. Calcd for C₄₁H₃₂N₂O₃S: C, 77.82; H, 5.10; N, 4.43; S, 5.07. Found: C, 77.42; H, 5.54; N, 4.07; S, 5.37.

7-(2-(5-Bromofuran-2-yl)vinyl)-9,9-diethyl-*N,N*-diphenyl-9*H*-fluoren-2-amine, mixture of *E/Z* (4b).

It was prepared from ((7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)methyl)triphenylphosphonium bromide (**4a**) and 5-bromofuran-2-carbaldehyde as described above for **1b**. The crude product was used in the next step without further purification.

5-(2-(7-(Diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)vinyl)furan-2-carbaldehyde (4c).

It was synthesized by the same procedure as described above for **1c**. The cis-to-trans isomerization was achieved by reflux with iodine (50 mg) in toluene (10 mL). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.61 (s, 1H), 7.76-7.72 (m, 3H), 7.63 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 3.9 Hz, 1H), 7.32-7.23 (m, 5H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.11-7.09 (m, 4H), 7.07-7.01 (m, 3H), 6.77 (d, *J* = 3.7 Hz, 1H), 2.11-1.93 (m, 4H), 0.36 (m, *J* = 7.3 Hz, 6H). MS (FAB) *m/z*: 509.2 (M⁺).

2-Cyano-3-(5-((E)-2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)vinyl)furan-2-yl)acrylic acid (4)

It was synthesized by the same procedure as described above for **1**. ^1H NMR (400 MHz, acetone- d_6): δ 7.98 (s, 1H), 7.77-7.70 (m, 3H), 7.59-7.55 (m, 2H), 7.42 (d, J = 3.7 Hz, 1H), 7.32-7.25 (m, 5H), 7.14-7.01 (m, 8H), 6.80 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, THF- d_8): δ 164.1, 161.7, 161.4, 161.0, 155.6, 152.5, 151.7, 149.1, 149.0, 148.5, 143.0, 138.7, 137.1, 132.8, 131.1, 129.6, 129.4, 127.8, 126.7, 126.1, 126.0, 125.7, 125.2, 124.4, 124.1, 123.7, 122.8, 122.5, 122.3, 121.5, 121.3, 120.7, 119.8, 119.2, 116.4, 110.6, 108.8, 98.7, 57.1, 33.3, 32.1, 9.6, 8.6, 8.3. MS (FAB) m/z : 576.2 (M^+).

1. (a) C. Y. Chen, S. J. Wu, C. G. Wu, J. G. Chen, K. C. Ho, *Angew. Chem, Int. Ed.* **2006**, *45*, 5822. (b) C. Y. Huang, Y. C. Hsu, J. G. Chen, V. Suryanarayanan, K. M. Lee, K. C. Ho, *Sol. Energy Mater. Sol. Cell* **2006**, *90*, 2391. (c) K. M. Lee, V. Suryanarayanan, K. C. Ho, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2398.
2. M. J. Plater and T. Jackson, *Tetrahedron* **2003**, *59*, 4673.
3. Y.-H. Kim, Q. Zhao and S.-K. Kwon, *J Polym Sci Part A: Polym Chem.* **2006**, *44*, 172.
4. K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu and K.-C. Ho, *Chem. Commun.* **2005**, 4098.

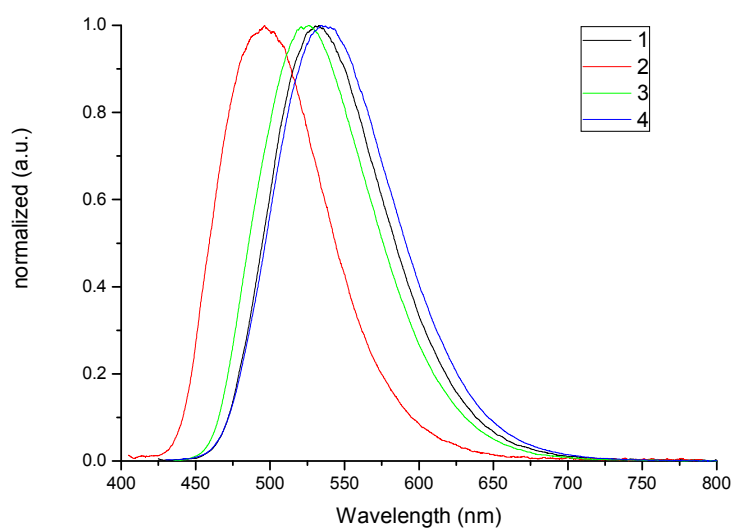
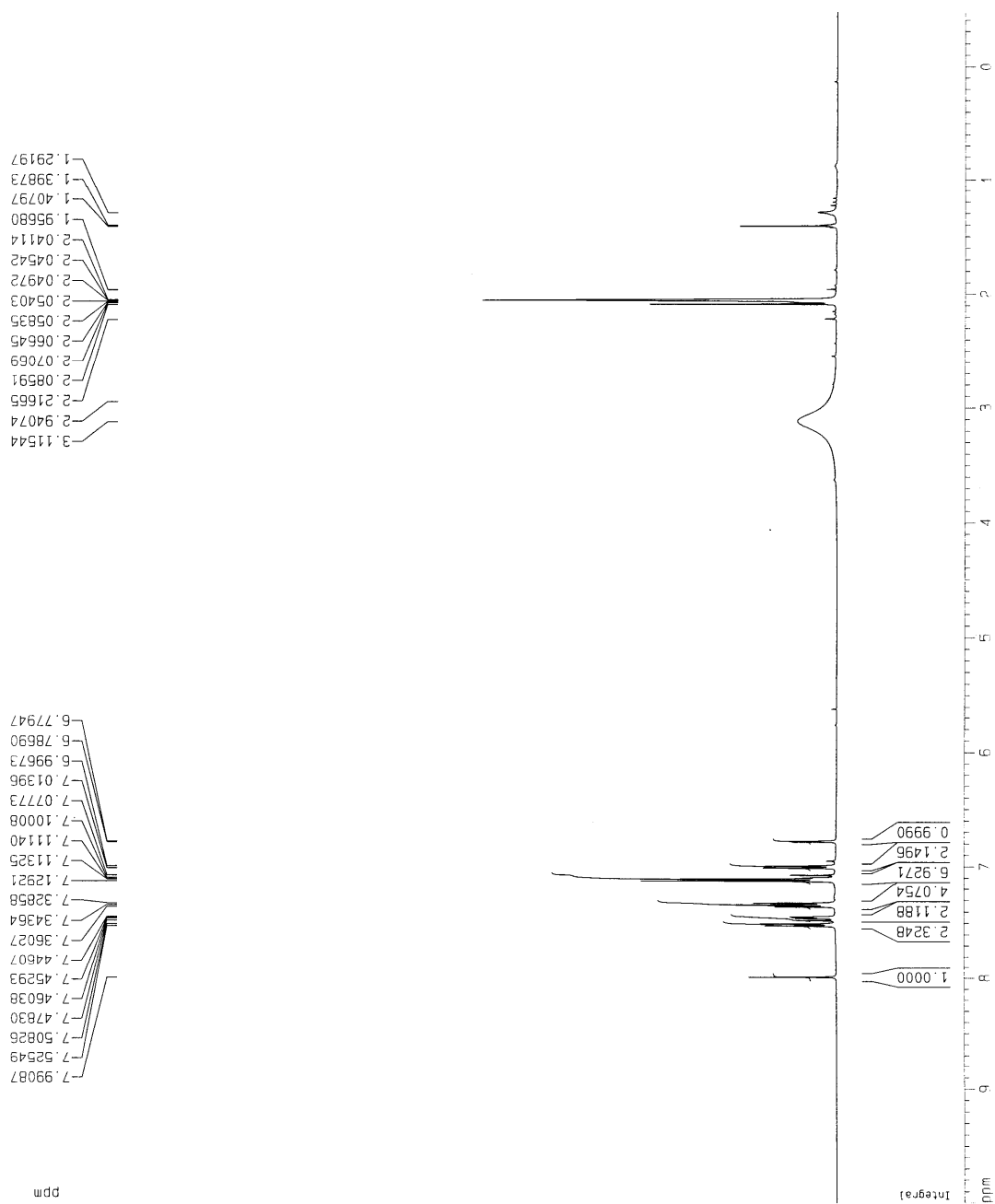
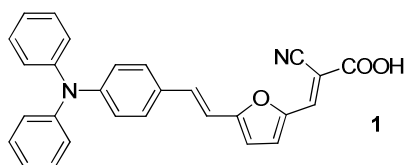
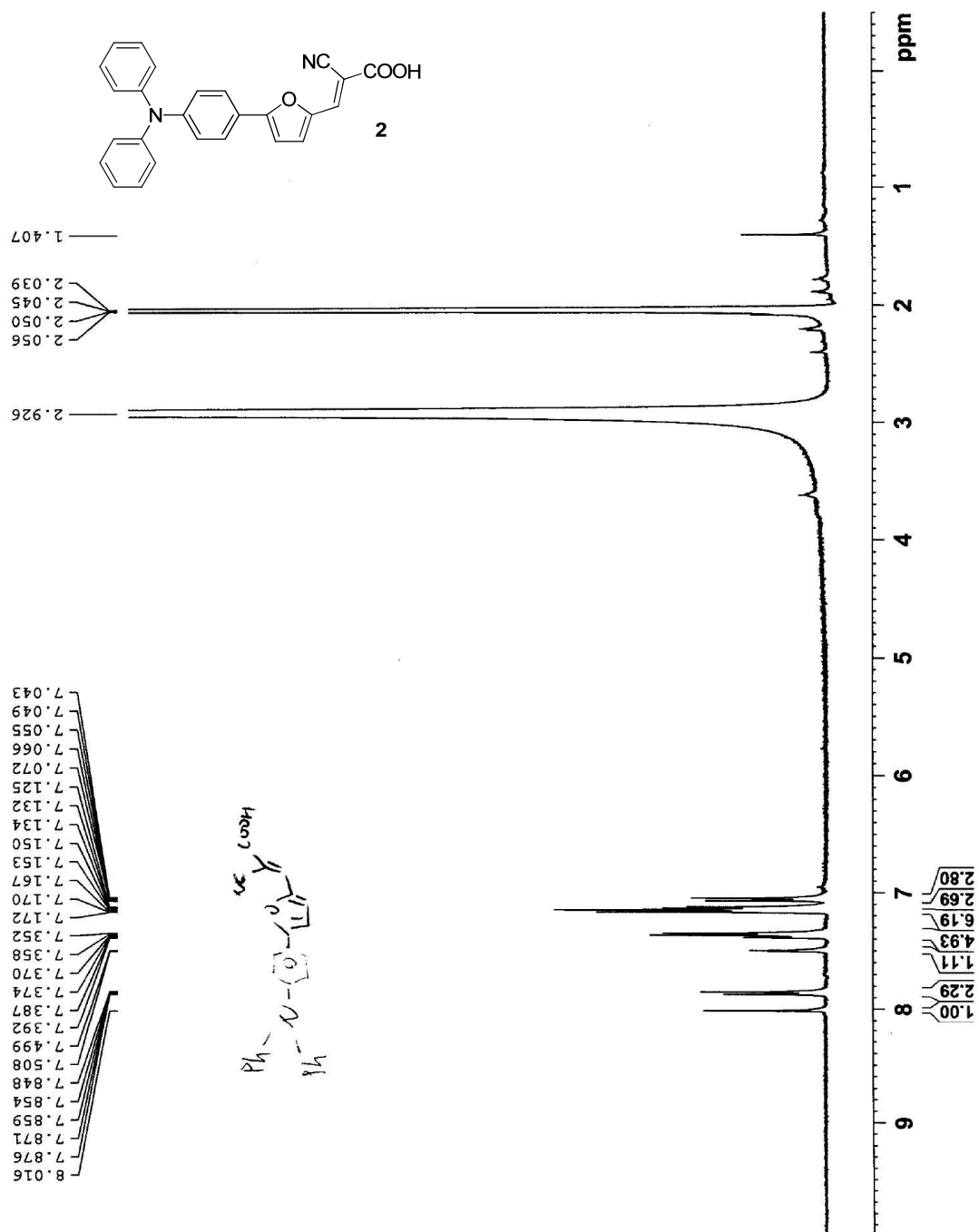
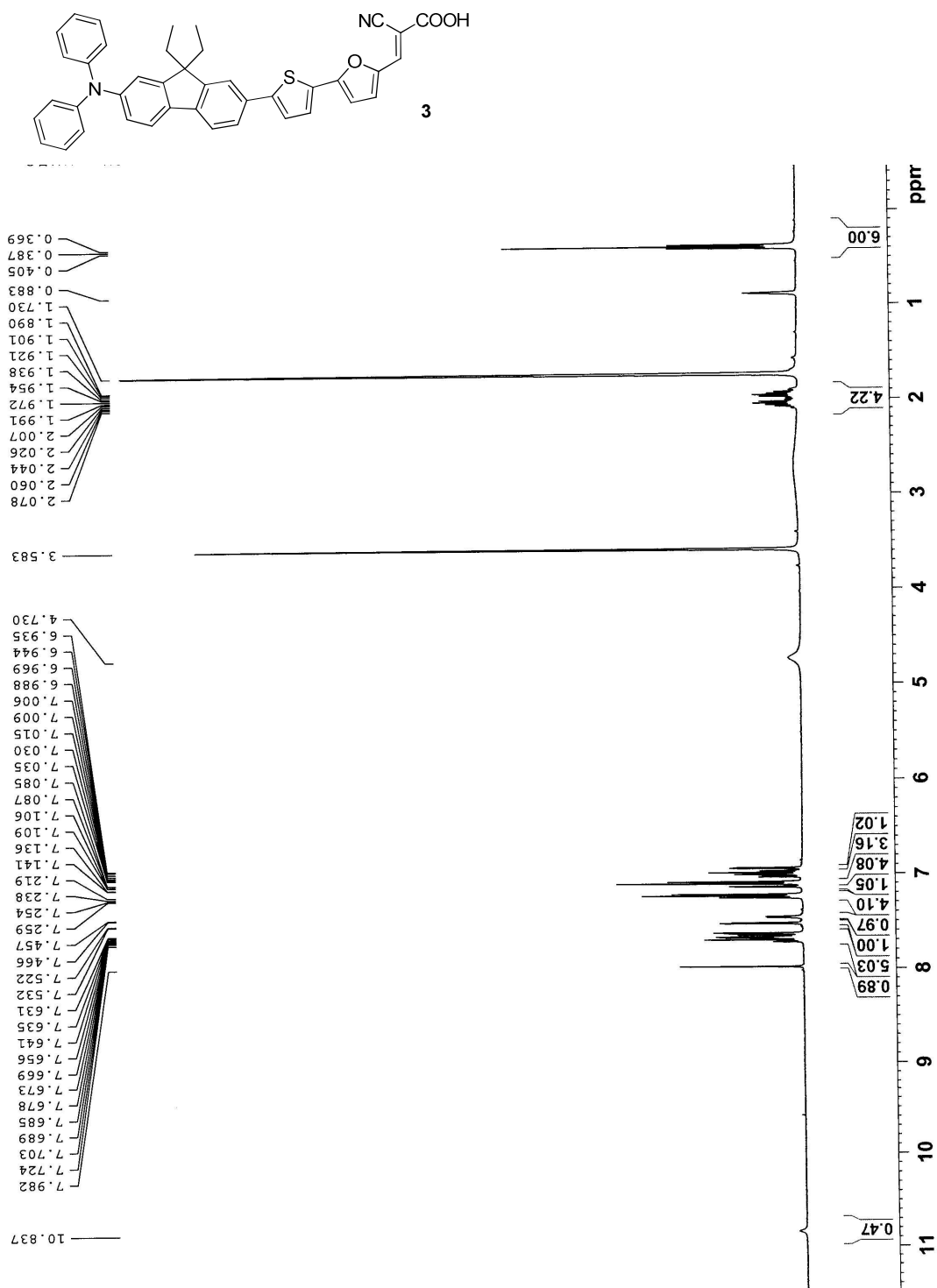
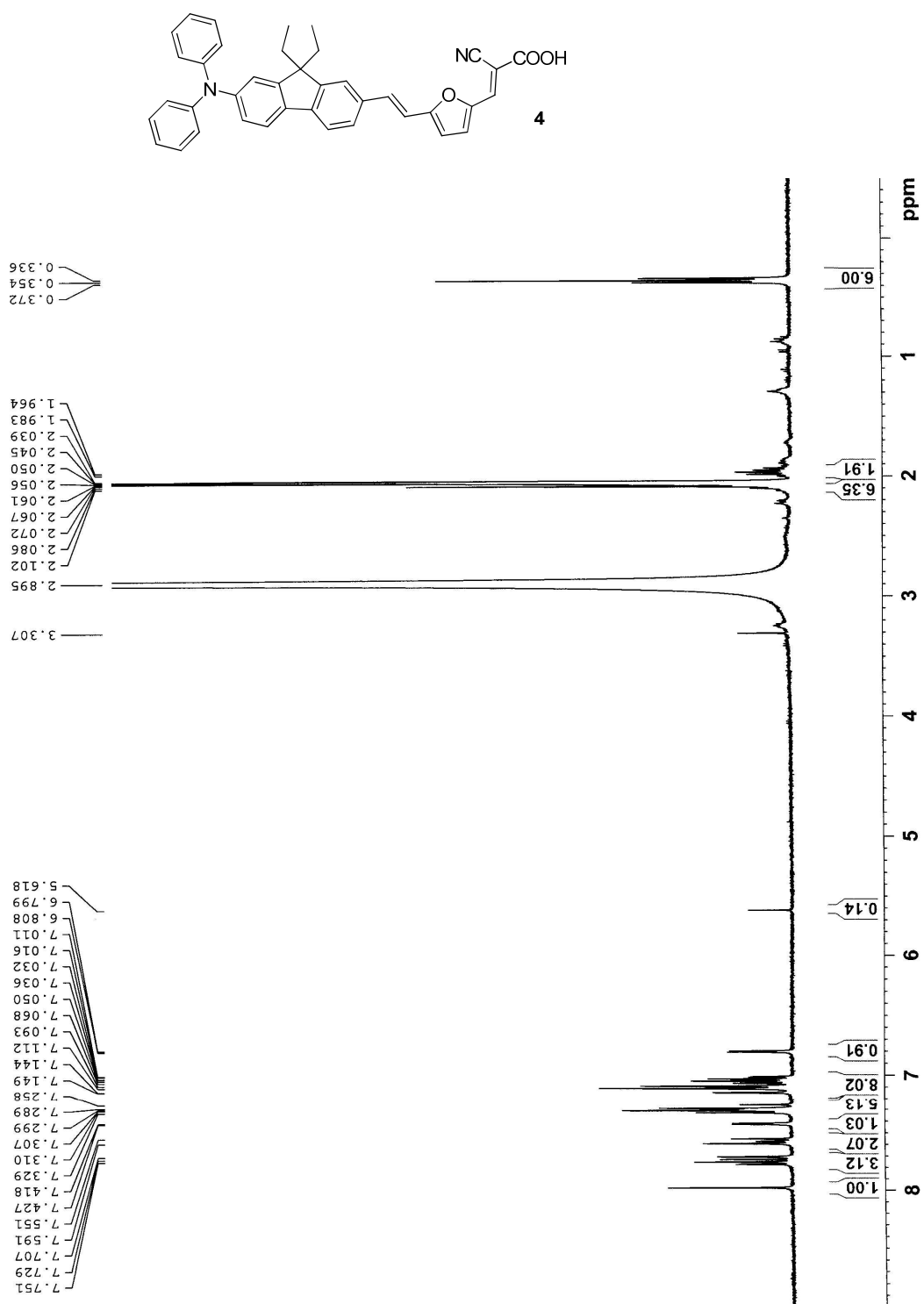


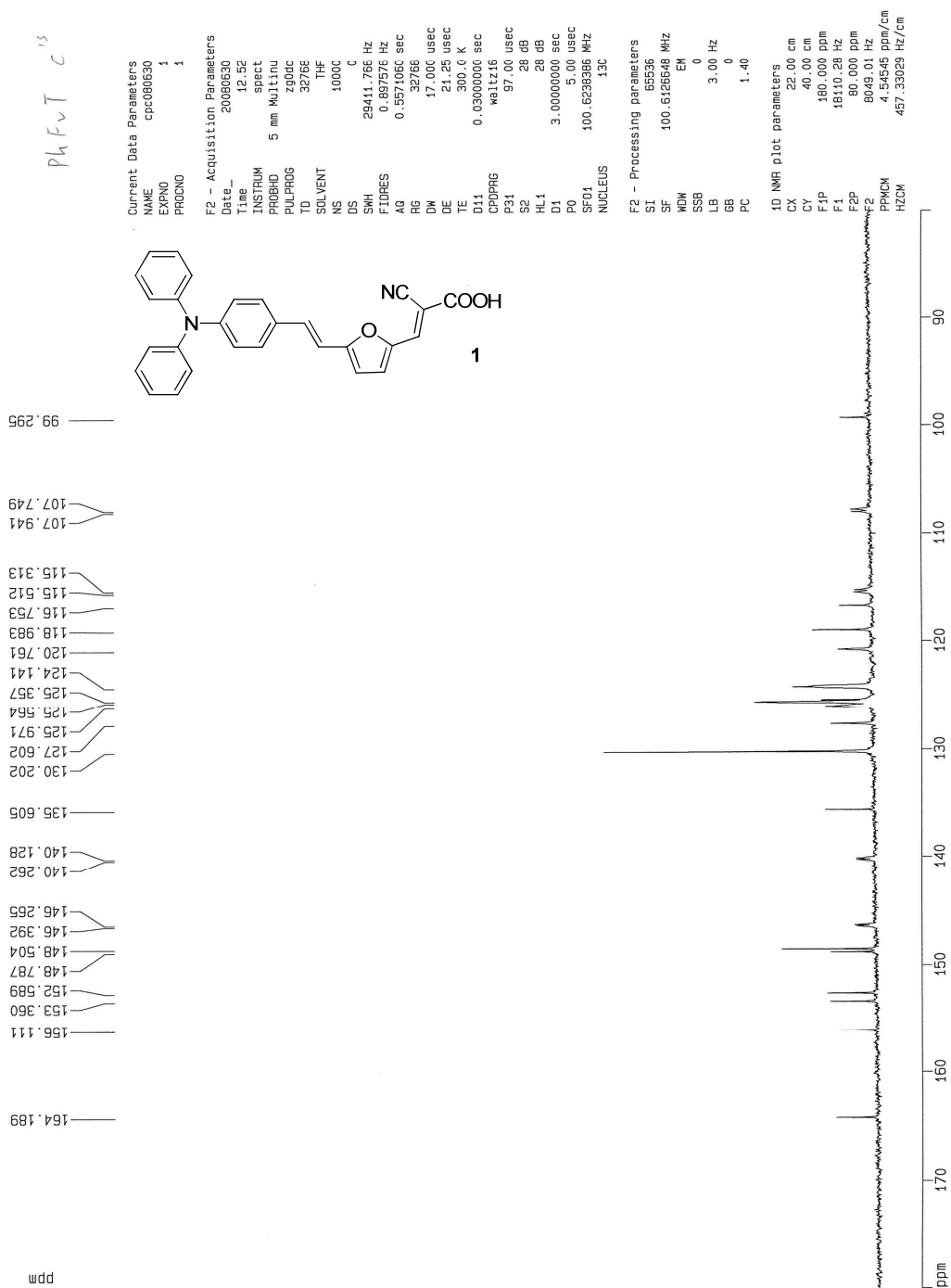
Figure S1. Emission spectra of dyes recorded in THF











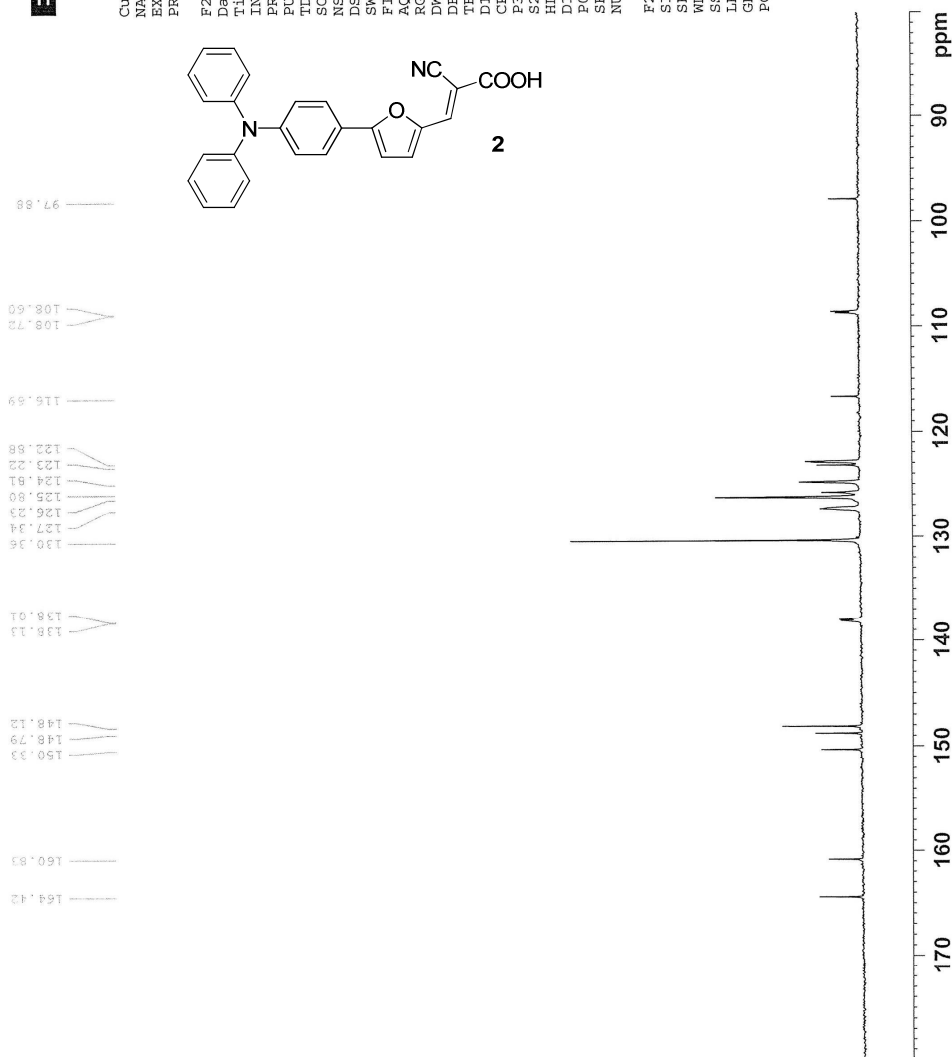
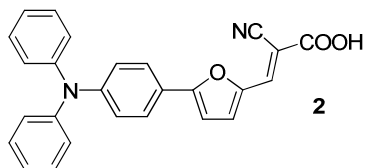
II. PhF ¹³C



Current Data Parameters
NAME cpc080626
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080627
Time 5.05
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpgdc
TD 32768
SOLVENT THF
NS 9601
DS 0
SWH 29411.766 Hz
FIDRES 0.897576 Hz
AQ 0.5571060 sec
RG 32768
DW 17.000 usec
DE 21.25 usec
TE 300.0 K
D11 0.03000000 sec
CPDPRG waltz16
P31 97.00 usec
S2 28 dB
HL1 28 dB
D1 3.00000000 sec
P0 5.00 usec
SFO1 100.6238386 MHz
NUCLEUS 13C

F2 - Processing parameters
SI 6556
SF 100.6126653 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40



Fluor C¹³



Current Data Parameters
NAME cpc080418
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080419
Time 4.45

INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30

TD 32768
SOLVENT CDCl₃-THF
NS 16416

DS 0
SWH 29411.766 Hz
FIDRES 0.897576 Hz

AQ 0.5571060 sec
RG 32768
DW 17.000 usec

DE 21.25 usec
TE 300.0 K
D11 0.0300000 sec

CFDPRG waltz16
P31 97.00 usec
S2 28 dB

HL1 28 dB
D1 3.0000000 sec
P0 5.00 usec

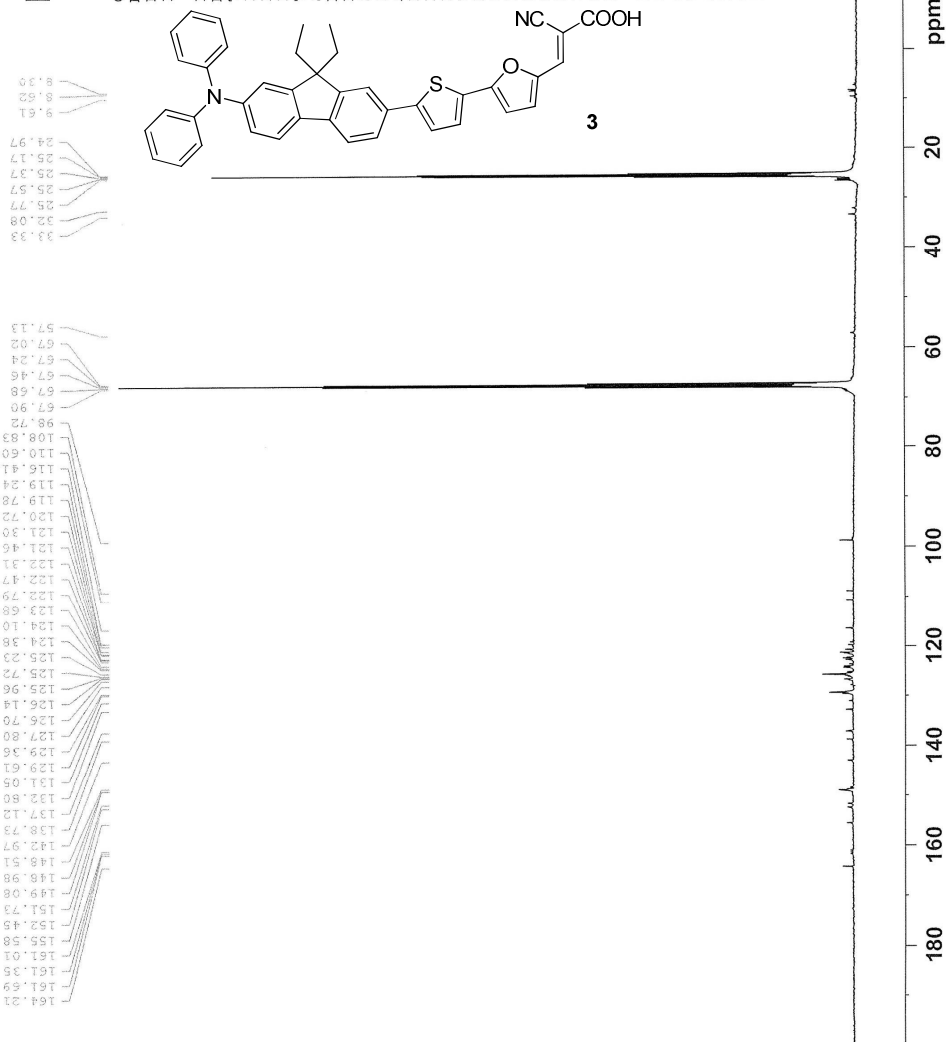
SFO1 100.6238386 MHz
NUCLEUS 13C

F2 - Processing Parameters
SI 65536
SF 100.6126646 MHz

WDW EM
SSB 0
LB 3.00 Hz

GB 0
PC 1.40

DPA-flu-s-v-cA



Fluor C¹³



Current Data Parameters
 NAME cpc080418
 EXPNO 13
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20080419
 Time_ 4:45
 INSTRUM spect
 PROBHD 5 mm Multinu
 PULPROG zgpg30
 ID 32768
 SOLVENT CDCl₃-THF
 NS 16416
 DS 0
 SWH 29411.786 Hz
 FIDRES 0.897576 Hz
 AQ 0.5571060 sec
 RG 32768
 DW 17.000 usec
 DE 21.25 usec
 TE 300.0 K
 D1 0.03000000 sec
 D11 waitz16
 CPDPRG 97.00 usec
 P31 28 dB
 S2 28 dB
 HL1 28 dB
 D1 3.00000000 sec
 P0 5.00 usec
 SFO1 100.623386 MHz
 NUCLEUS 13C
 F2 - Processing parameters
 SI 65536
 SF 100.6126646 MHz
 WDM EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

12PA-flu-s-o-c8

